UDC 666.1.01:666.1.031:66.046.52

COMBINED EVALUATION OF THE ROLE OF IMPURITIES AND SMALL ADDITIVES IN GLASS PRODUCTION

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Translated from Steklo i Keramika, No. 8, pp. 22 – 24, August, 2000.

The role of impurities and small additives in the production of high-quality glass articles is considered. Certain reactions that are possible under oxidizing and reducing melting regimes are demonstrated. Certain conditions for the use of cullet are considered, and its reducing potential is evaluated.

Under contemporary conditions a production enterprise has to manufacture competitive products for both the domestic and the international market. That is why development of a quality management system and satisfaction of international product quality standards are top-priority goals.

In this context, the quality parameters that characterize the external appearance of products are of special importance. One such parameter is the glass color shade, which can be quantitatively appraised based on the light transmission and the dominant wavelength in the visible spectrum range. The latter parameters depend directly on the content of pigment impurities and small additives introduced in the batch composition. Systematic studies of the behavior of impurities and small additives in glass technology make it possible to develop scientifically justified production elements, including input material control, the batch composition, decolorizing, tinting, and flame and electric melting of glass.

The quality of domestic raw materials is significantly inferior to foreign materials with respect to their impurity content. Considering also the transportation, storage, and pretreatment of materials at glass factories, it should be stated that each day one encounters materials with unstable content of impurities, moisture level, and granulometric composition, while the quality of recyclable cullet, especially cullet purchased from other enterprises, leaves much to be desired. In spite of an input control system, several parameters systematically fail to be evaluated.

Let us consider the parameters that need to be controlled and the ways their effect on the production process can be evaluated.

These parameters primarily include coloring impurities of ferric and chromium oxides, organic inclusions, as well as special additives introduced into glass to compensate the damaging effects of impurities: oxidizers (nitrates, sulfate, and oxides of arsenic, cerium, antimony, etc.), reducing agents (carbon, organic inclusions, etc.), and products of corrosion of current-conducting metallic materials (molybdenum, steel, etc.) in electric melting. In order evaluate the effect of these impurities and small additives, it is necessary to systematically monitor and regulate the content of impurities in raw materials, the redox characteristics of materials and glass batches, the melting conditions and regimes, and possible chemical modifications and reactions in the glass melt depending on the melting conditions. All this will make it possible to develop scientifically justified batch compositions and compositions of decolorizing and tinting mixtures for various melting conditions and to provide the required glass properties.

Let us consider some production examples and glass tint regulation schemes based on an analysis of published papers and our experimental studies.

It is known that ferric and chromium oxides are undesirable impurities that are regulated for sand, dolomite, chalk, and potash. For certain grades of clear household glass and cut crystal, the actual content of colorant iron impurities is within the limits of 0.023 – 0.040%. This quantity and the rather wide interval are related to the unstable content of impurities in sand and carbonate materials (chalk, dolomite).

The purest sand supplied by the Novoselovskii Mining-and-Concentration Works (Ukraine) with an iron oxide content of 0.015% is not inaccessible to many factories, since custom duties and railway expenses bring the price up to 800 rubles per ton or more. Consequently, manufacturers use less pure sand grades in which the iron oxide content amounts to 0.025% or more, and such sand is used in production although it is known to create problems in decolorization and clarification of glass. Up-to-date technologies for sand concentration provide sand with a ferric oxide content below 0.01%, and yet, implementation of this technology is being delayed, and supplies of this material are expected only in 2001. At the same time, the sand concentration tech-

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nology used at the Chaplyginskoe deposit gives hope for obtaining sand of the required quality.

Available carbonate materials are sufficiently pure. Thus, Novgorod and Zhiguli chalk contains no more than 0.02% Fe_2O_3, and Kovrov dolomites contain 0.06 – 0.07% Fe_2O_3.

Glass container factories, even the leading ones, in producing clear glass use sand whose impurity content ranges from 0.03 to 0.08 wt.%, lime powder with an iron content up to 0.15%, and purchased glass cullet in which ferric oxide impurities can reach 0.1% or more. Metallic and organic inclusions are found as well. With such quality of materials, it is hard to expect a stable and resistant color tint in glass.

Most factories use input control of materials with respect to coloring impurities. However, later the materials are crushed, dried, and sifted, as the consequence of which the initial composition is modified. Materials often arrive in railway cars contaminated with organic impurities, materials are carbonized in drying, and in crushing, materials get enriched in metals. The content of organic and carboniferous impurities in the course of material processing is not controlled. Therefore, in developing a batch formula, it is necessary to take into account the processed-material composition, rather than the composition determined in the course of the input control.

It is important to evaluate the redox potential of the materials and the batch as a whole. Studies of the Research and Development Institute of Glass in this field revealed the need for such control in production of household and container glass [1 – 7]. Methods for evaluating the redox potential were developed, and the need for substantiated rather than empirical adjustment of the batch composition based on the state of the materials was demonstrated.

The content of oxidizing or reducing agents can be estimated as well based on the possible reactions in melting, especially in the stage of silicate formation. Therefore, in developing the melting regime, one should provide for conditions of maximum-oxidation reactions of iron impurities, organic inclusions, sulfurous admixtures, and possible products of metallic-electrode corrosion.

Under oxidizing conditions, all possible reactions should be shifted to the right:

$$Fe^0 \xrightarrow{O_2,\, O^{2-}} Fe^{2+} \xrightarrow{O_2,\, O^{2-}} Fe^{3+};$$

$$C \xrightarrow{O_2} CO_2\,;$$

$$S^{2-} \xrightarrow{O_2,\, O^{2-}} S^0 \begin{cases} \xrightarrow{O_2,\, O^{2-}} S^{4+} \\ \xrightarrow{O^{2-}} S^{6+} \end{cases};$$

$$Mo^0 \xrightarrow{O^{2-}} Mo^{6+}.$$

Melting under reducing conditions is a more complex process. In the stage of silicate formation, the reducing flame, the batch composition, and the presence of oxidizers contradict each other. Therefore, the production of highly transparent household glass forbids melting under reducing conditions.

In production of clear container glass, it is necessary to pay special attention to the choice of materials and optimization of fuel combustion, especially in the silicate formation stage. Therefore, it is inadvisable to use sodium sulfate in large quantities for melting clear container glass when the iron content exceeds 0.03%. In practice, decolorization of glass with an iron impurity content exceeding 0.3% calls for introduction of oxidizers, and in the case of an increased sulfate content, the process requires reducing agents. Reducing reactions can lead to the emergence of small bubbles (flies) [8].

Furthermore, with an increased content of iron oxide impurities (over 0.03%), the tint shade necessarily deteriorates due to the formation of more intense coloring ions and complexes $[Fe^{3+} – Fe^{2+} – S^{2–} – O^{2–}]$. Therefore, under the conditions of a reducing flame it is more expedient to use a soda batch, when carbon is not introduced, and a reducing type of batch is excluded. Yet even in that case, in order to obtain a good color shade in the silicate formation stage (the first pair of burners) it is recommended that an oxidizing type of flame be maintained.

Cullet admixtures, especially cullet brought from other industrial enterprises, have a substantial effect on the glass tint. One bottle factory got a new cullet supplier, other conditions being equal, and began using broken sheet glass in production. In spite of the fact that sheet glass has a lower iron oxide content than bottle glass (0.08 and 0.13%, respectively), in using broken sheet glass, the color shades of the finished glass deteriorated and became less stable, the light transmission decreased, and small bubbles (fly) emerged. The reasons were identified only after determining and correlating the parameters of iron oxide reduction

$$P = FeO/(FeO + Fe_2O_3)$$

in the sheet glass cullet and in the finished bottle glass. The reduction parameters of these glasses were 15.6 (sheet glass) and 22.5 (bottle glass). In the course of this investigation, sulfide sulfur was identified in the sheet glass, which passed over to the bottle glass composition. In this particular case, considering the degree of iron reduction and the presence of sulfide sulfur, the cullet can be regarded as a reducing additive, which makes the following reactions possible:

$$Fe^{3+} \xrightarrow{\text{cullet}} FeO \text{ (light blue shade)};$$

$$S^{6+} \xrightarrow{\text{cullet}} S^{4+} \to S^0 \to S^{2-};$$

$$\left.\begin{matrix} Fe^{3+} \\ Fe^{2+} \end{matrix}\right| \xrightarrow{S^{2-}} \left|\begin{matrix} \text{Colorant} \\ \text{complexes} \end{matrix}\right| \text{(brown shades)}.$$

The above reactions resulted in the emergence of small bubbles, modification of tints, decreased light transmission, thermal inhomogeneity of the glass and, consequently, the appearance of such defects as nonuniform thickness and in-

sufficient heat resistance of the bottles. In order to prevent such phenomena, it is necessary to pay closer attention to cullet quality and not allow uncontrolled use of cullet. In this connection, we recommend determination of the redox potential, the sulfide sulfur S^{2-} content, and organic impurities of cullet. It probably makes sense to introduce a calculated quantity of a reducing agent into the batch composition, in order to balance the reducing effect of the cullet, to maintain the existing redox potential of the glass melt, and thus to avoid the emergence of bubbles. Such recommendations should be done individually for each particular case. By studying local conditions and carrying out corresponding calculations, it is possible to solve the problems of long-term use of cullet and regulate the batch compositions. The Research and Development Institute of Glass can be of assistance in this respect.

Since the problem of preparation, purification, and stabilization of cullet is now widely discussed, we would like to draw attention not only to the impurities and granulometric composition of cullet, but to its thermal history as well, which should be taken into account and related to the accepted parameters of glass bottle production. Of special interest in this context are the latest publications by specialists from the Moscow Electric Lamp Works [9], who stress the need to expand the number of quality-related parameters that have to be registered in the technological documentation. This is a topical issue for Russian manufacturers, who are significantly behind Western European companies in this respect.

Let us consider some typical changes occurring in glass when its composition contains reducing additive that penetrate into the glass as a result of corrosion of conducting materials, for instance, molybdenum.

Regarding molybdenum as an active reducing additive in the glass melt, it is possible to represent a possible direction of the redox processes during electric melting as follows:

$$Mo^0 \xrightarrow{O^{2-}} Mo^{6+};$$

$$Fe^{3+} \xrightarrow{Mo} Fe^{2+};$$

$$S^{6+} \xrightarrow{Mo} S^{4+} \rightarrow S^0 \rightarrow S^{2-}.$$

Apparently, the reactions of reduction of sulfur and iron are intensified in the presence of molybdenum, and a large quantity of oxidizer is needed to compensate for the effect of molybdenum [10]. The calculation of the oxidizer content should be carried out taking into account the minimum corrosion (oxidation) of molybdenum.

Thus, impurities and additives, in spite of their small quantities, have a substantial effect on a number of quality parameters, properties, and melting conditions. Therefore, in production of high-quality household and container glass, it is necessary to provide monitoring of the materials, the technological process, and the product in all stages. In doing so, special attention should be paid to determination of the redox potentials of the material, batch, and cullet.

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